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Mechanical Testing of Silica Phenolic Composites at Elevated Temperatures

Prepared by R. D. CARNAHAN
Materials Sciences Laboratory

October 1968

Laboratory Operations
AEROSPACE CORPORATION

Prepared for SPACE AND MISSILE SYSTEMS ORGANIZATION
AIR FORCE SYSTEMS COMMAND
LOS ANGELES AIR FORCE STATION
Los Angeles, California

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FOREWORD

This report is published by the Aerospace Corporation, El Segundo, California, under Air Force Contract F04701-68-C-0200.

The author is grateful to C. Lander, Avco Corporation, for pertinent private communications.

This report, which documents research carried out from December 1967 through June 1968, was submitted on 4 November 1968 to Lieutenant Jerry J. Smith, SMTTM, for review and approval.

Approved

W. C. Riley

W. C. Riley Director
Materials Sciences Laboratory

Jerry J. Smith

Jerry J. Smith, 2nd Lt, USAF
Project Officer

ABSTRACT

The principal objective of this study was to determine the mechanical properties, tensile yield, ultimate strength, and Young's modulus of elasticity of a silica fabric reinforced phenolic composite at temperatures above the cure level. The proposed application for this class of material as an ablative liner of a rocket nozzle skirt extension requires such engineering data for temperatures ranging up to $3000^{\circ}F$ so that design safety margins can be based on a thermostructural analysis.

Testing was carried out on samples taken from the three principal directions of a tape-wrapped conical frustum, i.e., hoop, parallel-to-ply, and perpendicular-to-ply directions, at temperatures ranging from 75° to $3000^{\circ}F$. For all three directions, the strength showed an initial decrease up to $\sim 1000^{\circ}F$ followed by a plateau extending up to the softening point of silica ($2200^{\circ}F$) beyond which the strength dropped further. A minimum in the modulus curve for the hoop orientation is believed to be associated with the transition of virgin phenolic to char and corresponds to dimensional changes noted in the thermal expansion behavior.

CONTENTS

FIGURES

I. INTRODUCTION

The successful application of advanced composite materials to component design and manufacture generally requires a substantial physical measurement effort to determine mechanical and thermal properties of the composite. The wide variety of structural morphologies of composites and the physical geometries of designs will furthermore often influence the properties of the material under consideration. It is, therefore, not only appropriate but advisable to study the properties of samples removed from prototype hardware if feasible. In this manner the production processes, such as tape wrapping and vacuum bagging, whose variability effects the properties of the composite, are used, and their influence is reflected in the physical property determination. Thus a more meaningful and reliable engineering analysis can be generated.

During the planning stages of this study, it became apparent that insufficient data was available from open sources to specify the properties of silica phenolics over the temperature range of interest for any principal direction, i.e., hoop, parallel-to-ply, or perpendicular-to-ply. In fact, it was found that no reliable data existed for the direction perpendicular to ply.

This study was established therefore for the purpose of generating the engineering stress-strain properties of silica phenolic for all three principal directions, from room temperature to $\sim 3000^{\circ}F$. Of importance also was the simulation of, as nearly as practicable, time rates of heating paralleling those of a rocket engine environment. The experimental results indicate silica phenolic to be generally a well behaved enginerring material in terms of mechanical behavior. An indication of a minor anomaly appears in the temperature region of virgin-to-char transition, which is apparently dictated by chemical reactions in the resin.

II. EXPERIMENTAL PROCEDURE

A. MATERIAL HISTORY

The silica phenolic used in this investigation was fabricated by the Haveg-Reinhold Company using Sil-Temp square weave silica fabric having a 40 × 30 thread count and Monsanto Company's SC-1008 phenolic resin. The silica fabric is preimpregnated with resin, slit to tape, and wrapped warm about a mandrel at 150 deg to the centerline such that the warp fibers are oriented in a circumferential direction. The fabric having been wrapped to a thickness of approximately 2 in., the assembly is debulked by vacuum bagging, heating, and application of pressure for removal of excess resin until a thickness of about 1.5 to 1.75 in. is achieved. Subsequent to removal from the mandrel, the assembly is postcured to a maximum temperature of 320°F and machined to a thickness of 0.750 in. The resulting material has an average density of 110 lb/cu ft (1.75 g/cc), a resin content of 34 wt%, and residual volatiles totaling 1.62 wt%.

The tape-wound assembly thus formed produces an orthotropic material with three mutually perpendicular directions regarded as principal material directions, among which the mechanical properties show significant variations. These directions are the hoop, parallel-to-ply, and perpendicular-to-ply, the latter two being through the 0.75-in. thickness.

B. TENSILE TESTING

The maximum material thickness of 0.75 in. necessitated the design and fabrication of substandard minature tensile samples having a nominal overall length of 1 in. with a 0.5 × 0.125 × 0.125 in. gage section as shown in Fig. 1. The shrinkage of the material at temperatures above 1000°F imposed a further restriction in testing and precluded clamping of the tab ends. For alleviation of this difficulty, a set of 0.5-in.-diam thoriated tungsten rods were spark machined and provided a wedge action seat to accept the sample ends. Alignment was obtained through the use of universal joints, and the

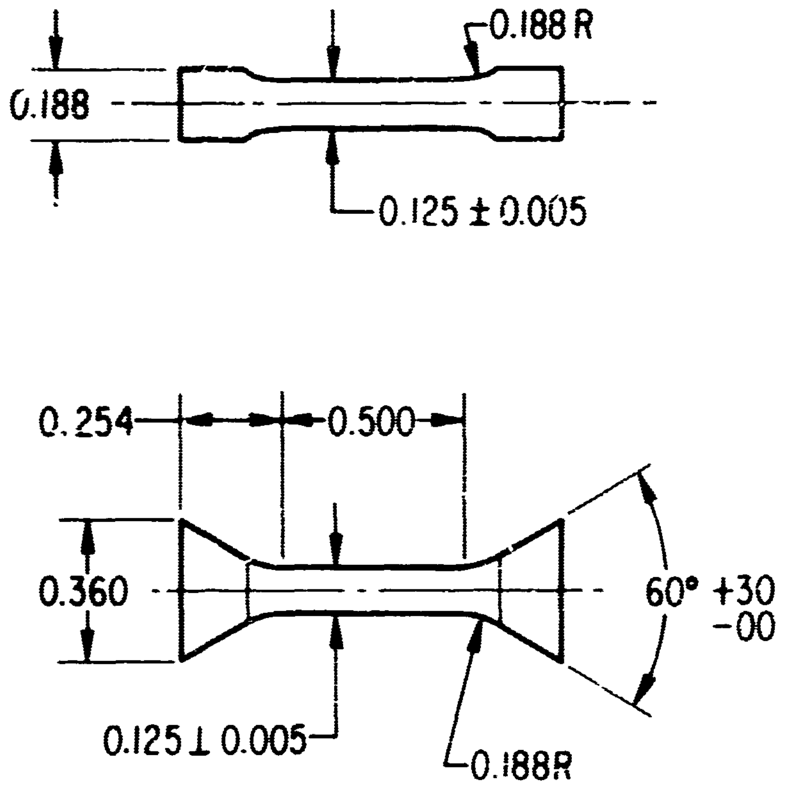

Figure 1. Tensile Sample Configuration

entire assembly was mounted within a vacuum furnace containing a tantalum resistance heating element. The chamber was evacuated and purged with purified argon a minimum of three times before elevated temperature testing in an argon environment was initiated. Temperatures were monitored both with a Pt-Pt-10% Rh thermocouple mounted with the bead in contact with the sample surface and with a micropyrometer. Above 2500°F. all temperatures were determined optically with an error of ± 10°F.

The furnace assembly was mounted in a table model Instron, and mechanical testing was carried out at a cross head travel rate of 0.05 in./min. A typical high temperature run required 2.5 to 3.5 min from initial application of power to the furnace. In all cases a 30-sec soak time was used at temperatures permitting thermal equilibrium to be established. Load cycling at a level of 5 to 10% of the tensile strength was used during heatup for maintenance of sample alignment.

C. ELASTIC MODULUS

A new approach for determination of tensile modulus was dictated by the absence of suitable high temperature extensometry for microtensile samples. The wedging action between test sample and grip combined to give the characteristics of a soft tensile machine, and thus the initial portion of the recorded load-deflection curves could not be relied on to give a Young's modulus value. The technique developed consisted of a cyclic loading and unloading of the sample between 5 and 50% of ultimate load. In this manner, it was found that a perfectly elastic hysteresis was developed within a few full cycles as shown in Fig. 2. The slope of this curve, a system modulus, was demonstrated to be directly proportional to the modulus by instrumentation of samples with bonded foil strain gages. The latter use of strain gages also permitted the determination of the proportionality constant for a given direction. System modulus values were thus determined for each of the principal material directions by use of both temperature point-by-point measurements with individual samples and by continuous measurements on a single sample at a variety of temperature points, and with good correlation.

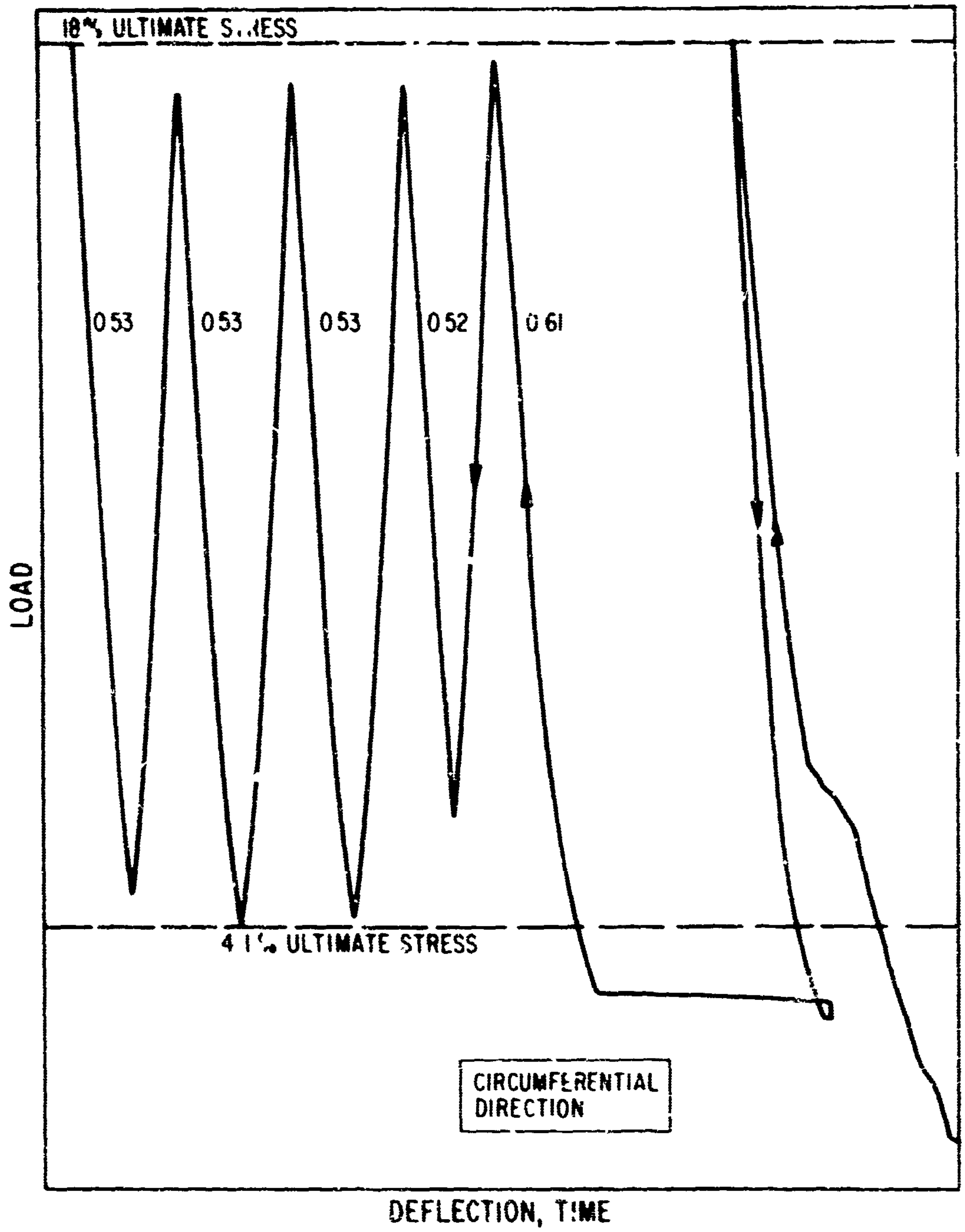

Figure 2. Typical Cyclic Loading Curve to Obtain Modulus

D. THERMAL EXPANSION

Thermal expansion measurements were made by means of a standard Leitz dilatometer with quartz components and a heating rate of $33^{\circ}F/min$. Because of the marked contraction characteristics in the transition region, cylindrical test samples 0.125-in. diam by 0.125 in. long were used. Experiments simulating higher heating rates were conducted by preheating the furnace to $2000^{\circ}F$ and then sliding it over the sample test assembly. In this manner it was possible to achieve measured average heating rates in excess of $1000^{\circ}F/min$.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The results of the tensile testing are shown in Figs. 3-5, in which the tensile yield strength,[1] tensile ultimate strength, and Young's modulus of elasticity are shown as a function of temperature. An early concern during this investigation was that a size effect problem might cloud the validity of data obtained on subscale test samples. This concern was alleviated, however, by the excellent agreement obtained with room temperature data points on two additional sample sizes and geometries of hoop orientation. These latter were standard ASTM 2-in. gage-length samples, one with a circular cross section and the other rectangular, tested in other facilities.

The agreement noted was obtained after a slight modification of the miniature hoop samples that consisted of a 50% reduction of the gage thickness, which eliminated shearing of the wedge-shaped gripping heads. This difficulty was not encountered with the parallel- and perpendicular-to-ply orientations. As an added precaution, however, small clips on radiation shields were attached to the tungsten pull rods to protect the sample ends from direct thermal radiation from the heating source. The slight drop in strength noted in the vicinity of 1000°F will be treated in the modulus discussion.

The trends shown for the temperature dependence of the tensile properties generally indicate the dominant influence of the silica phase in dictating the mechanical behavior. The initial drop in strength is consistent with previously reported data, although the strength is quite constant over a wide range of temperature up to the softening point of the silica. Above 2000°F the composites, particularly the hoop and parallel-to-ply orientations, exhibit substantial plasticity with tensile elongations of 20% and more. It is of particular interest to note that the perpendicular orientations, representing essentially the pure resin properties, exhibit a tensile strength of 40 psi at 2800°F. Families of typical stress-strain curves for the various orientations are shown in Figs. 6-8

[1] The tensile yield strength is defined in this study as the point of departure from the initial linear portion of the curve.

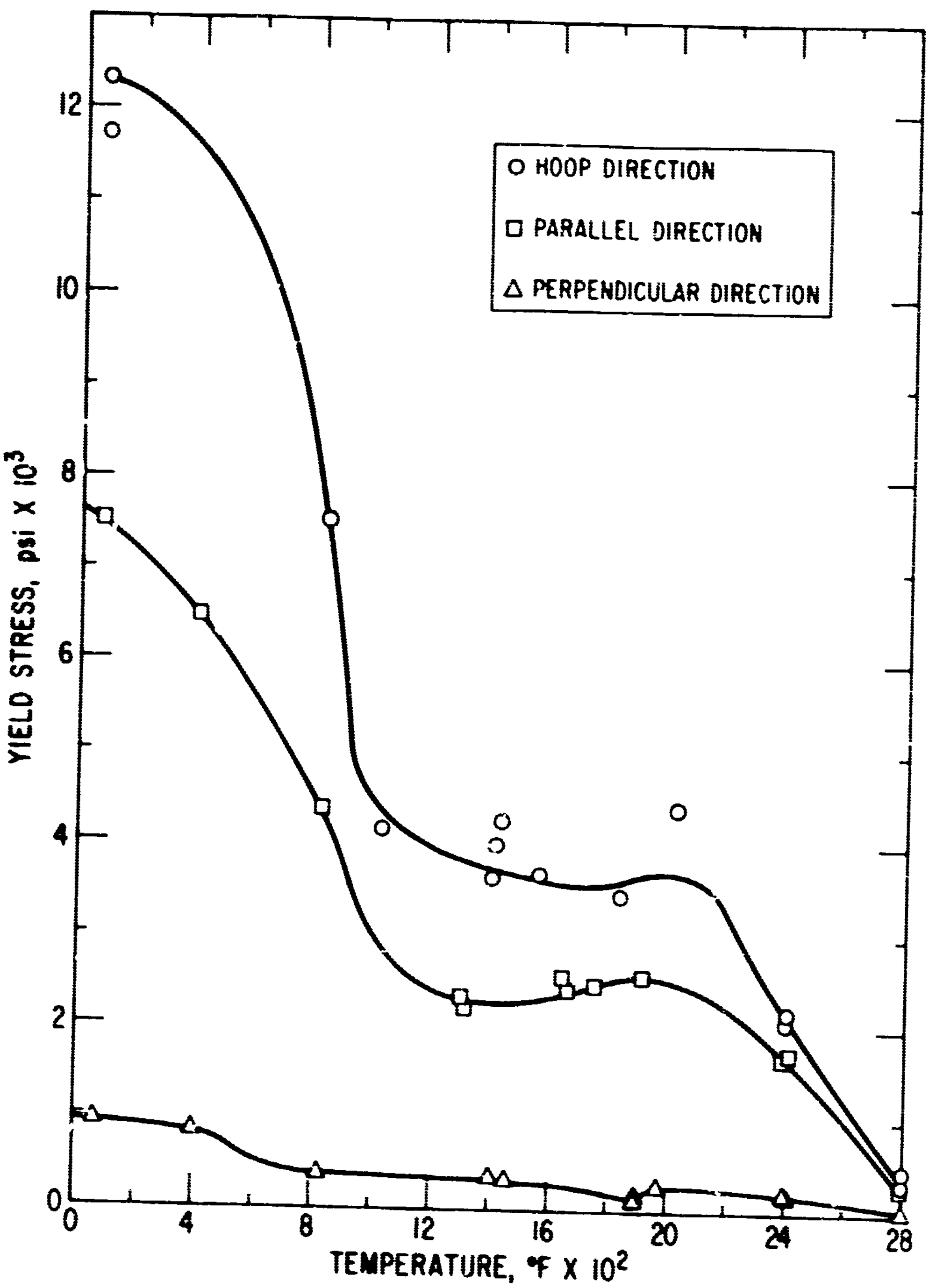

Figure 3. Tensile Yield Strength versus Temperature

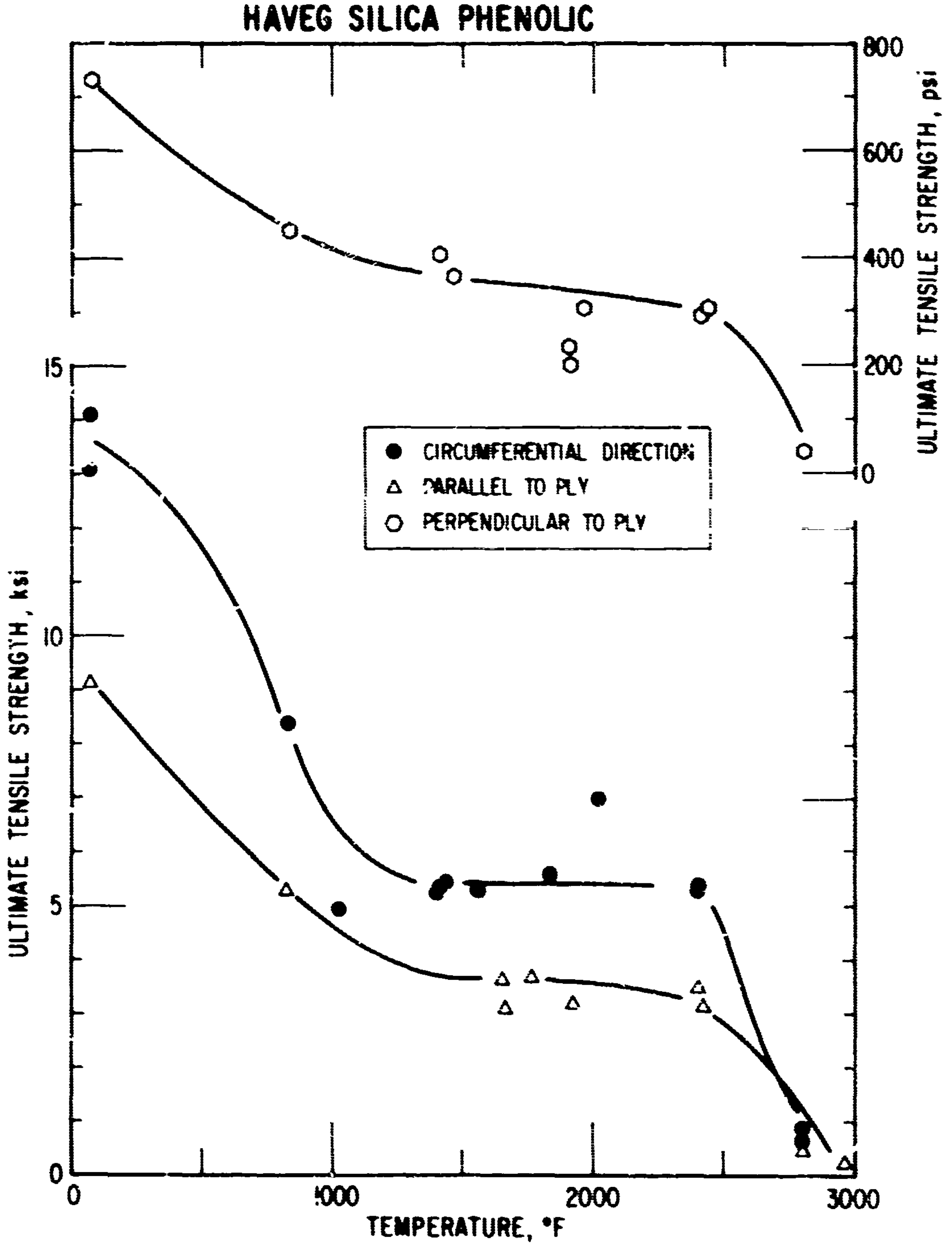

Figure 4. Tensile Ultimate Strength versus Temperature

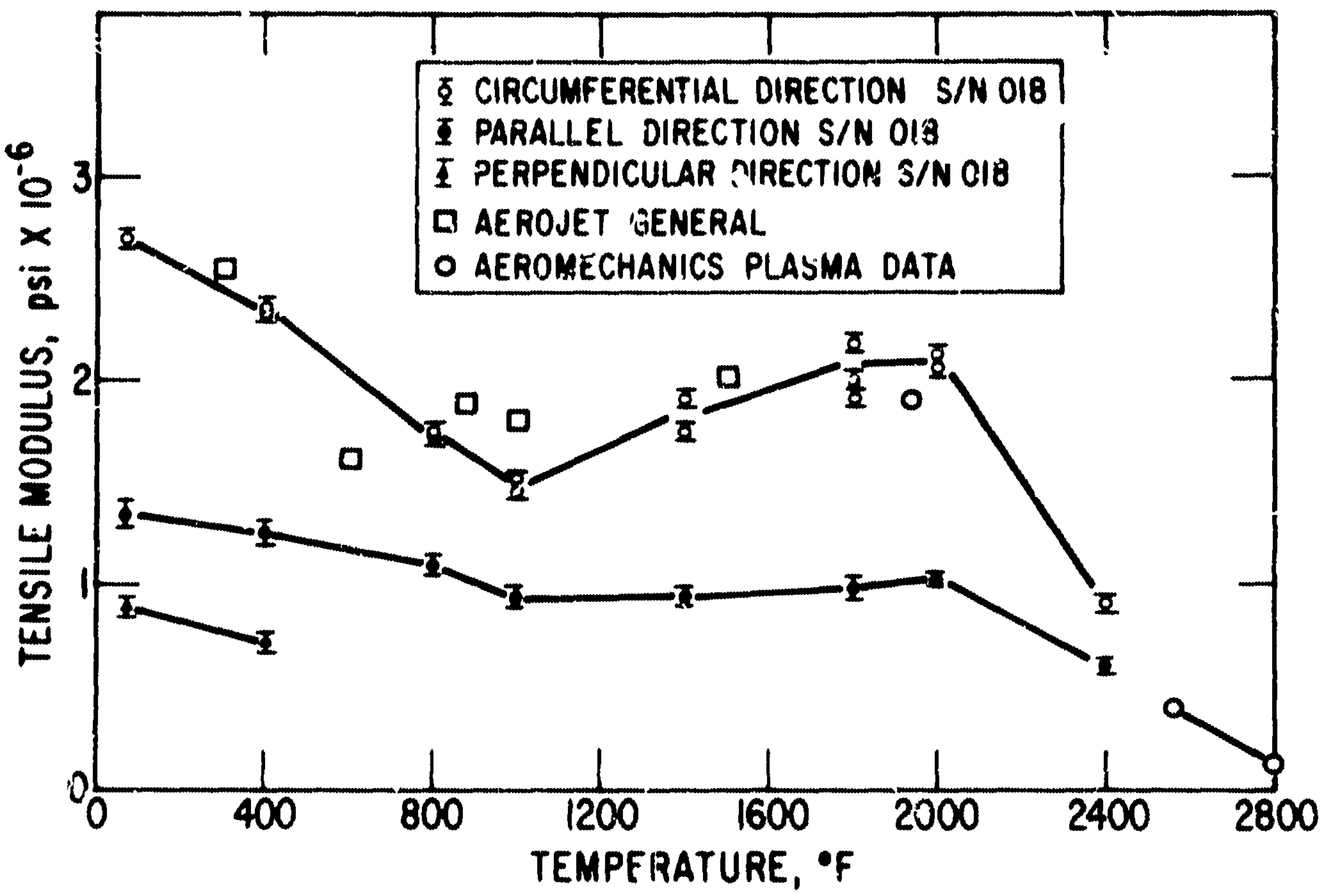

Figure 5. Young's Modulus versus Temperature

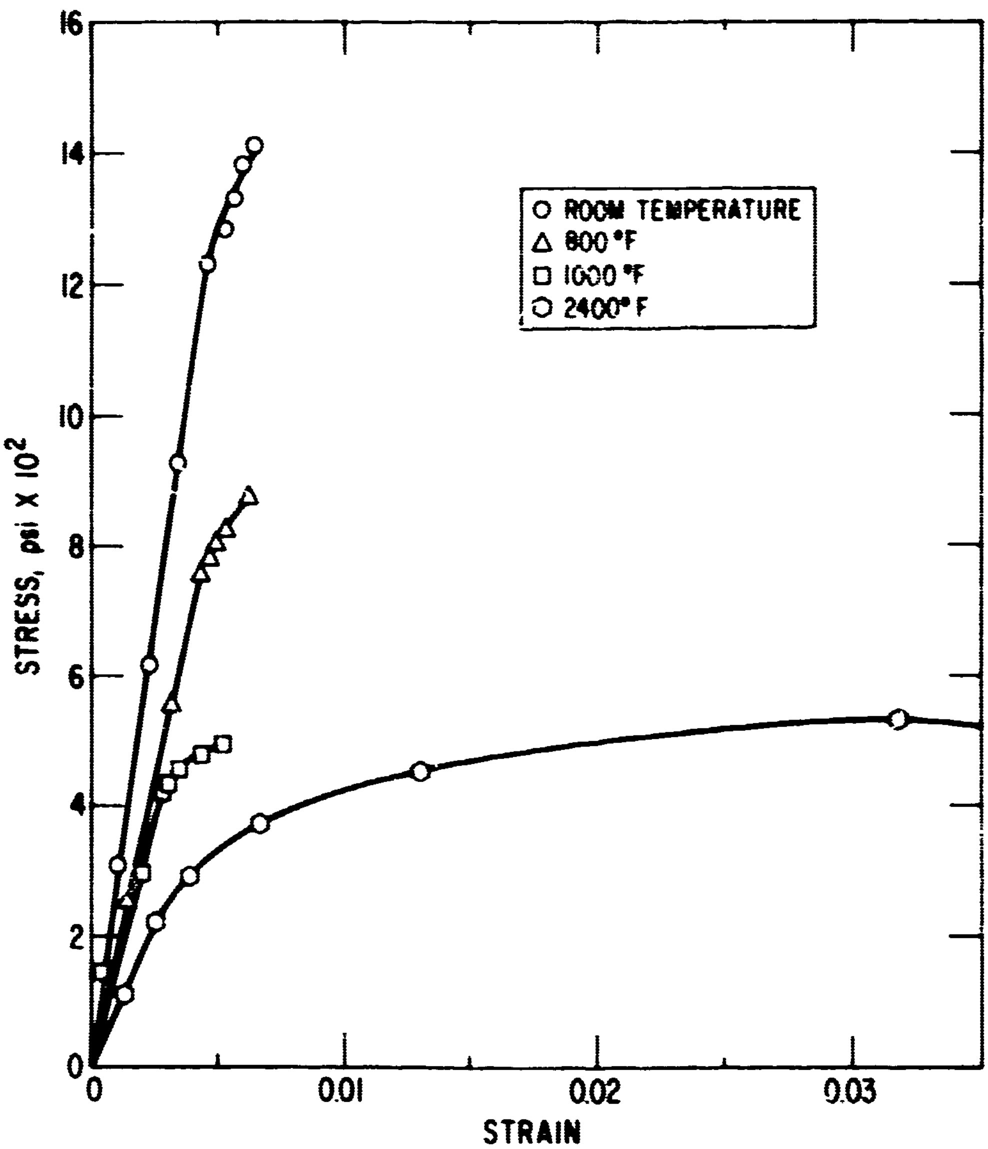

Figure 6. Typical Stress Strain Curves for Hoop or Circumferential Orientation

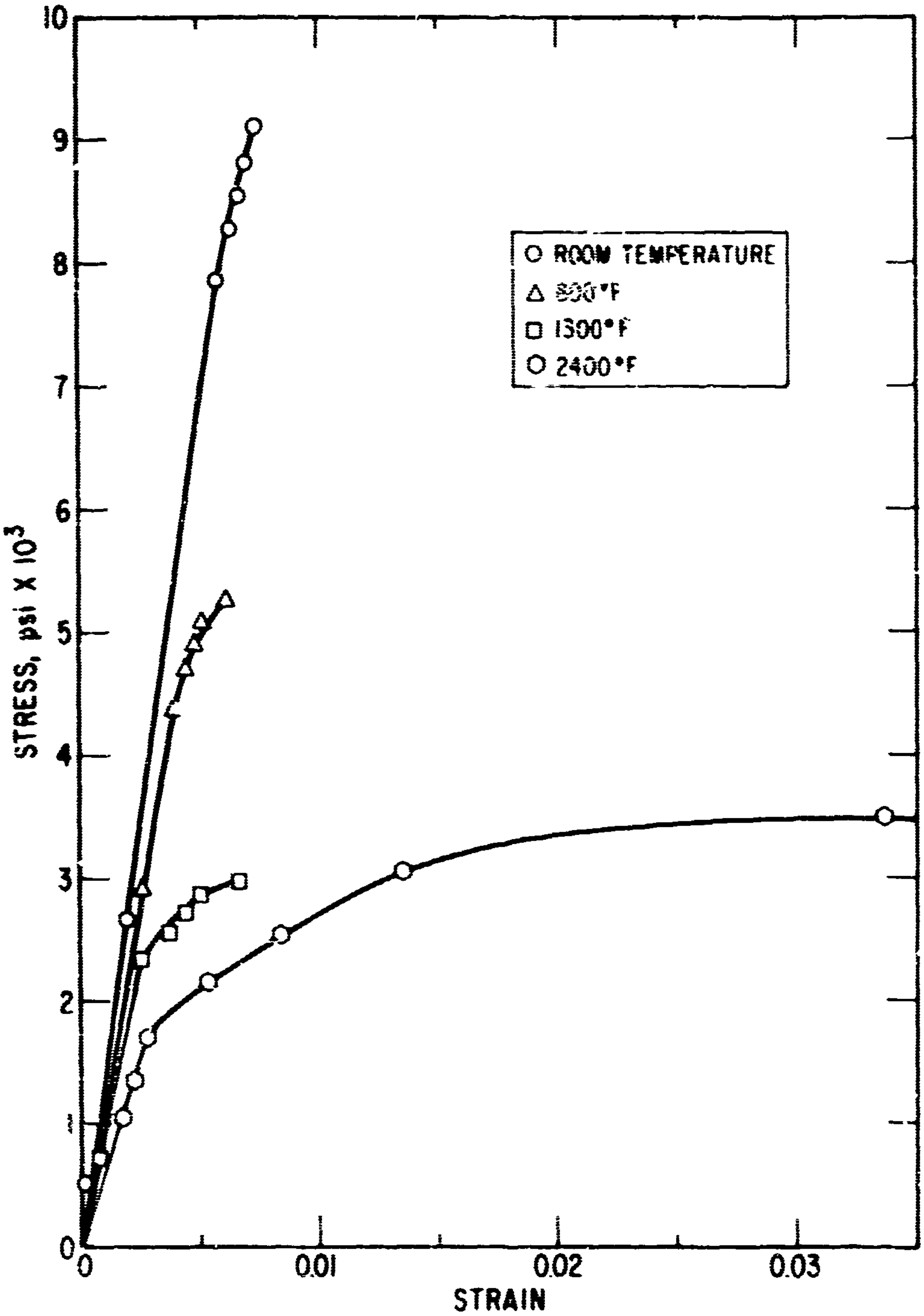

Figure 7. Typical Stress Strain Curves for Parallel Orientation

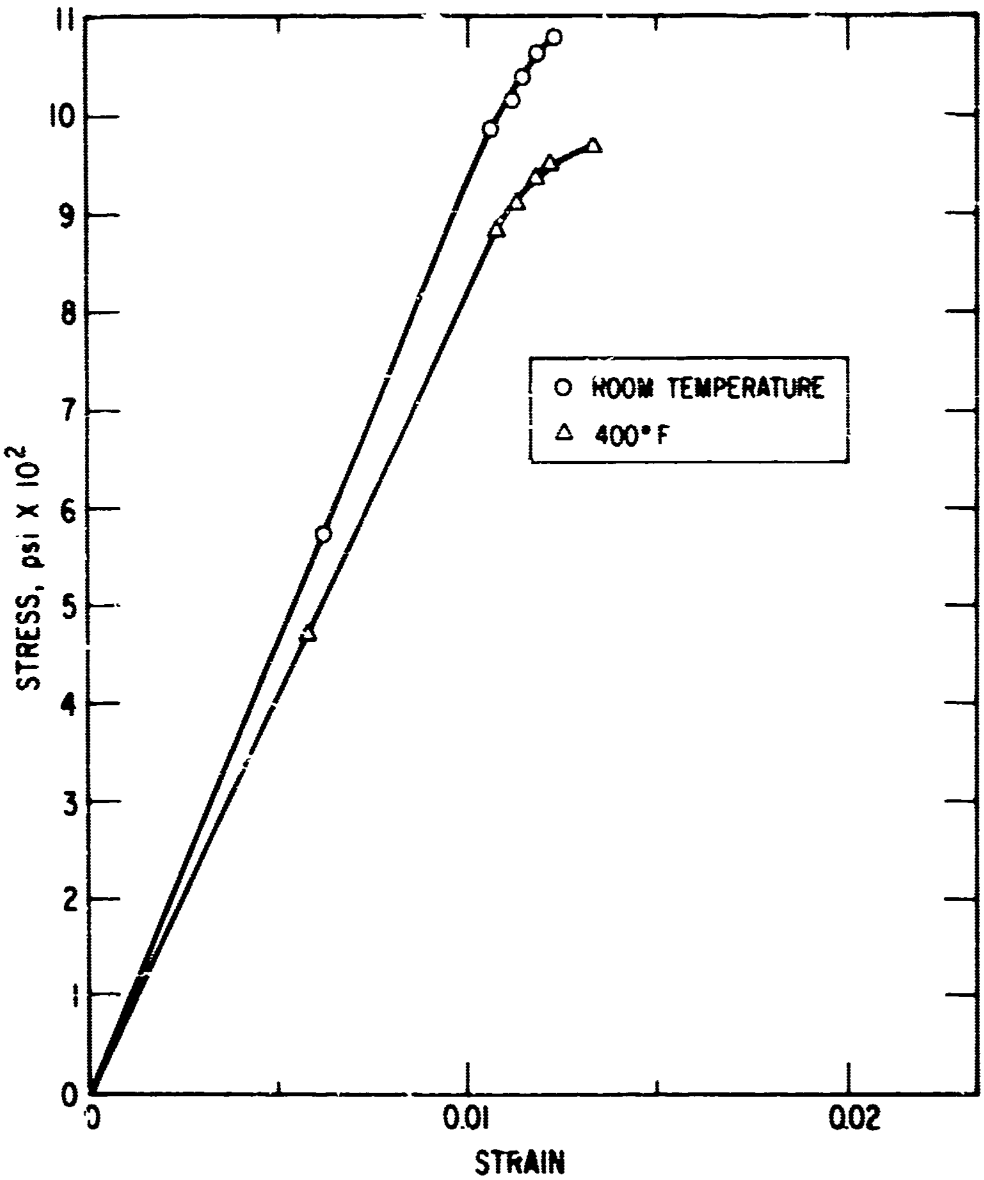

Figure 8. Typical Stress Strain Curves for Perpendicular Orientation

Perhaps the most interesting characteristics of the silica phenolic material were discovered during experiments to determine the Young's modulus. The technique described earlier was a continuous load-unload schedule in which the load never exceeded 50% of the tensile strength nor did it fall below about 10%. Tests conducted at room temperature with strain gages confirmed the assumption that the sample and rigid tungsten grip-rods constituted an elastic composite system with a characteristic modulus. The modulus for a given temperature was thus determined by the following procedure: (1) obtaining a system modulus at room temperature, (2) heating the sample to temperature, (3) determining again the system modulus, and (4) taking the product of the room temperature material modulus with the ratio of the system moduli at elevated temperature and room temperature. A further check on this approach was provided by independent measurements made on standard size hoop samples in two calibrate experiments, one covering the range from room temperature to 1500°F using clip on extensometer rods and the second from 2000° to 2900°F using photographic techniques. The data shown in Fig. 4 for the hoop direction are a composite of the data obtained using the technique outlines herein and the two independent studies mentioned above. The paucity of data for the perpendicular-to-ply orientation reflects the inability of this orientation to sustain a sufficient load in the load-unload schedule to permit use of this method above 600°F, at least for the sample sizes used in this study.

A surprising observation was that identical modulus results were obtained by a second procedure in which single samples were used to determine a system modulus at room temperature, 400°, 800°, 1000°, 1400°, 1200°, 2000°, and 2400°F for a given orientation. Not only were the modulus values consistent with those determined by single point-single samples but the tensile strengths determined at 2400°F subsequent to this prolonged heating schedule fell in line with the earlier tensile data suggesting no degradation of properties with extended step-wise heating times.

It is noted that the hoop orientation modulus shows a significant minimum at about 1000°F, which is also reflected to a lesser degree by a parallel-to-ply orientation. There are two possible explanations for this behavior.

The first considers that the heating rates and total times at temperature are sufficiently short that either no structural changes due to chemical reaction occur in the resin matrix or that changes taking place are minor. Thus the properties observed are those of a relatively "stable" amorphous structure heated to elevated temperatures. As the temperature is increased through the transition region, the kinetic processes and resulting structural changes dominate even for short times. The properties observed are those of a new material reflecting a more rigid and temperature-resistant matrix than the virgin material.

The second model considers that the chemical reactivity of the resin system, shown clearly by the thermal expansion characteristics of the perpendicular-to-ply orientation in Fig. 9, produces a degradation of the interfacial bond between the matrix and the reinforcement. The initial expansion, in reality a bloating caused by the resin pyrolysis and evolution of residual volatiles not removed by the relatively low temperature cure employed, is sufficient to disrupt structural continuity locally between matrix and reinforcement. The elastic properties for the hoop orientation then experience a decrease due to inability of the composite to effectively transfer shear stresses between matrix and reinforcement. As the temperature is increased further, the resin begins to shrink with the occurence of additional cross linking and charring. At 1400°F and above, for the times and heating rates employed, the shrinkage, as indicated by the thermal expansion behavior, exceeds the earlier expansion, and effective bonding between matrix and reinforcement is reestablished as evidenced by the increase in modulus. A further point in support of this concept is that the room temperature modulus, determined subsequent to a 2400°F cycle, shows an increase of nominally 20%. Above 2000°F, the silica reinforcement exhibits softening resulting in a gradual drop in E as the melting point is approached.

The less dramatic influence of chemical interface degradation on the modulus for the parallel-to-ply orientation is understandable from the nature of the fabric. The warp fibers experience a positive tension both during initial weaving and during composite layup and thus lie very straight in

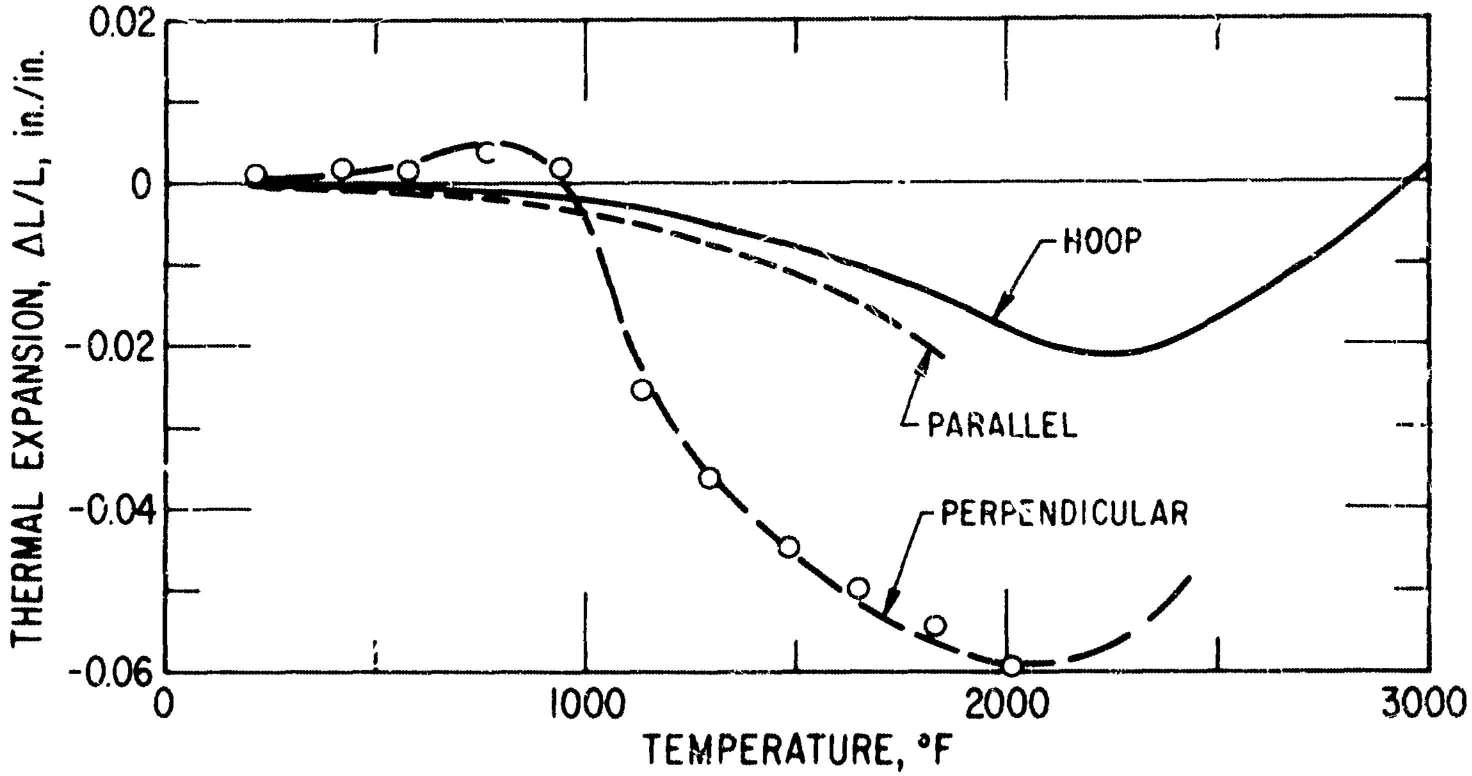

Figure 9. Thermal Expansion versus Temperature for all Orientations

contrast the fill fibers are woven into the warp under no tension and rove in and out defining an approximately sinusoidal path in the composite. Under the application of a tensile stress, both the effective length and volume of fill fiber are decreased by the random orientation resulting in a less significant interaction between matrix and fiber. The net effect is that the degradation of the interfacial bond exhibits essentially no influence on the parallel-to-ply modulus.

IV. MICROMECHANICS

While the primary purpose of this paper has been to present the method and results of testing silica phenolic composites at elevated temperatures, it was considered of interest to examine in a limited way the fit of the modulus data with current composite theory. As two typical theories, the work of Paul (Ref. 1) and Shaffer (Ref. 2) were selected. For the transverse properties, i.e., perpendicular to ply, Paul's expression for the lower bound is:

$$E_c = E_m E_f / (V_m E_f - V_f E_m) \tag{1}$$

where E_c, E_m, and E_f are the Young's moduli of the composite, modulus, and fiber, respectively, and V is the volume fraction. This particular expression applies to a unit cube with a transverse slab-like inclusion and thus should be representative of the transverse properties of an orthortropic composite. Using values of

$$E_m = 600,000 \text{ psi}$$
$$E_f = 10 \times 10^6 \text{ psi}$$

and $$V_f = 0.50$$

one obtains $$E_{transverse} = 1.133 \times 10^6 \text{ psi}$$

which compares with the experimental range of 835,000 to 944,000 psi. Shaffer has proposed the following expression for reinforcement volume fractions less than 0.68.

$$E_T = E_m \left[1 - \frac{(1 - E_m/E_f)(0.8247 V_f - V_f)}{1 - 0.8247 V_f (1 - E_m/E_f)} \right] \tag{2}$$

Substituting the same values for E_m, E_f, and V_f as used above one obtains

$$E_T = 904,000 \text{ psi}$$

Shaffer's approach yields a more exact agreement with experiment. It is based on a hexagonal array of fibers with a particular proportion of fibers and resin and assumes an average stress distribution. It is found that Shaffer's

general expression for a fiber content in excess of 68% is precisely the same as Paul's lower bound Eq. (1). An exact solution requires use of a method that would permit a treatment of the exact stress distribution over the entire surface.

The longitudinal constants, i.e., for the hoop and parallel-to-ply orientations, are obtained from the rule of mixtures by both Paul and Shaffer; however, Paul indicates its validity only for equivalent Poisson's ratios.

$$E_L = E_m V_m + E_f V_f \tag{3}$$

In testing the rule of mixtures it was decided to treat the warp and fill fibers independently, considering, in one case, an "effective" matrix consisting of resin plus fill fibers and, in the second case, resin plus warp fibers. Equation (2) was applied to determine the two new "effective" matrix moduli using the 40 × 30 thread count to establish the relative volume fractions of fibers:

$$V_{fw} = 0.288 \qquad V_{ff} = 0.217$$

The "effective" matrix values thus computed were

E_m (matrix plus fill fibers) - 610,000 psi

and

E_m (matrix plus warp fibers) = 660,000 psi

For the hoop orientation a value of 3.314×10^6 psi is predicted compared with experimental values of 2.65 to 2.74×10^6 psi suggesting that either the effective volume fraction of reinforcement is too high or that consideration of the effect of Poisson's ratio would yield a value closer to that observed experimentally. The latter possibility was tested with values of $\mu_f = 0.2$ and μ_m .44 with Paul's upper bound equation and resulted in a value of 3.08×10^6 psi, which is more consistent with the experimental value.

For the parallel orientation the former assumption, e.g., regarding the effective volume fraction of fibers, was invoked. Assuming a sinusoidal distribution of filler fibers as shown in Fig. 10 it is reasonable to consider that the effective fiber length and volume are reduced by 50%. Using Eq. (3),

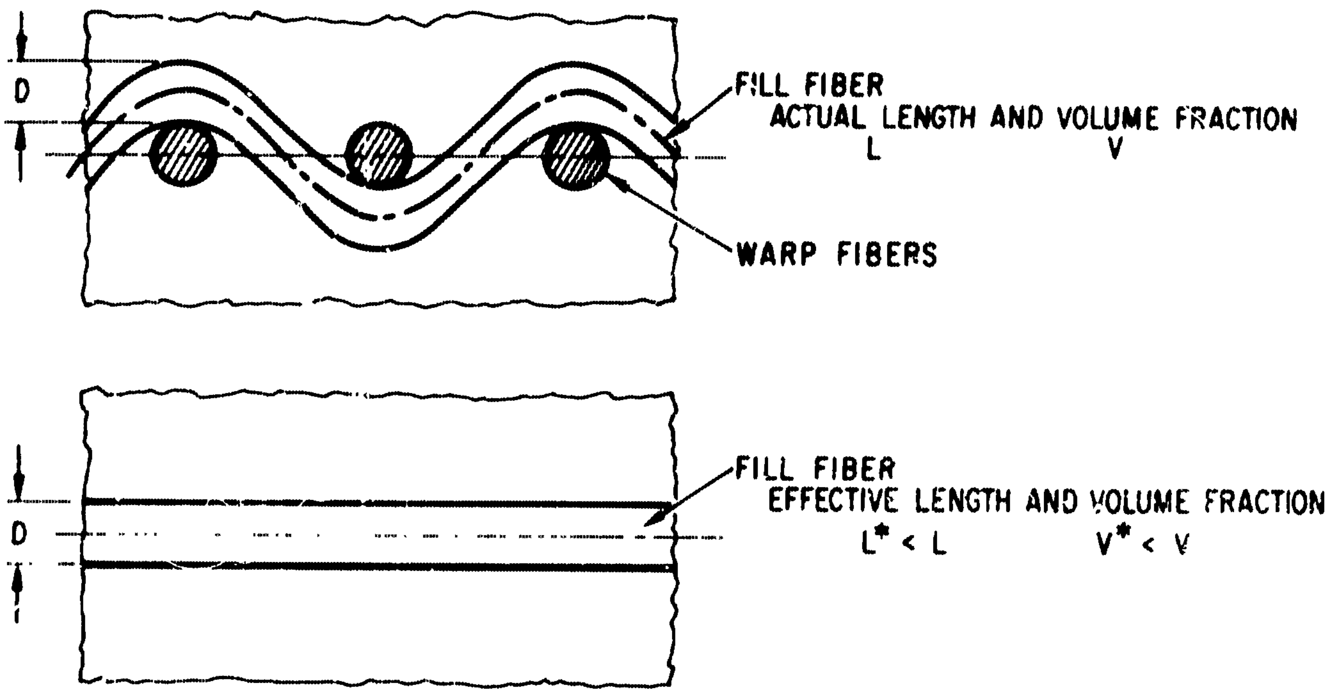

Figure 10. Representation of Effective Fiber Fraction for Fill Fibers

one obtains $E = 1.57 \times 10^6$ psi as compared with an experimental variation between 1.29 and 1.42×10^6 psi. Clearly, both the assumption of effective fiber fraction and consideration of Poisson's ratio bring the predicted values into closer agreement with experiment.

V. CONCLUSIONS AND RECOMMENDATIONS

While the mechanical testing of chemically unstable resin composite systems poses unusual problems, it has been demonstrated that such testing to at least 3000°F can be accomplished with modest facilities. The technique employed to determine Young's modulus at temperatures up to 2400°F does not require expensive extensometry or physical attachment to the test sample but must, however, be demonstrated to be applicable to a given system by experimental verification. The problems associated with sample shrinkage dictate the necessity of a load cycling capability, or its equivalent, sufficient to maintain alignment while heating and to prevent premature overloading of the sample. With standard laboratory procedures and special care given to sample fabrication and handling, the percentage of valid tests, with minimum scatter, can exceed 90%.

It can be stated on the basis of this study that the silica-phenolic system represents a well-behaved composite system with reasonably predictable properties. It was further demonstrated that with care the transverse orientation, representing essentially the resin properties, could be tested up to 3000°F where it sustained a load and exhibited a normal stress-strain behavior.

A minima in the modulus versus temperature curve at ~ 1000°F for the hoop orientation has been tentatively identified as having its origin in a degradation of the interfacial bond between resin and fiber during the resin transition from virgin to char. Its disappearance above 1400°F is attributed to char shrinkage about the fibers as evidence by the thermal expansion behavior. Further studies to elucidate this hypothesis would be of considerable interest.

Application of micromechanics theories of Paul and Shaffer to the silica-phenolic resin composite under consideration yielded reasonable agreement with experiment. It was required, however, to use both an "effective" matrix modulus and an "effective" fiber volume fraction assumption to achieve optimum results. Clearly, substantial room exists for further development of micromechanics composite theories that can mathematically model representations closer to the physical state of these materials.

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